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Potential of non-traditional isotope studies for bioarchaeology

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Abstract As a consequence of recent developments in mass spectrometry, the application of non-traditional stable isotope systems (e.g. Ca, Cu, Fe, Mg, Sr, Zn) as well as radiogenic isotopes to archaeological materials is now possible. These techniques have opened new perspectives in bioarchaeology and can provide information on metabolism, diet and the mobility of past individuals. This review demonstrates this potential and describes the principle of these new analytical approaches. In addition, we emphasize how the "non-traditional" stable isotope systems compare and contrast with classic isotopic analyses.

Keywords Archaeological sciences · Metal stable isotopes · Tracers · Diet · Mobility · Metabolism

Introduction

Notion of traditional and non-traditional isotopes

The notion of traditional and non-traditional isotopes is usually applied to stable isotopes, which remain stable through time, as opposed to radioactive isotopes that decay into a daughter isotope from a different element. This resulting daughter element is radiogenic. Radiogenic isotope abundances are typically expressed as the ratio of the radiogenic isotope of interest to a stable isotope of the same element (e.g. $^{87}Sr/^{86}Sr$). For stable isotope systems, the isotopic abundance is mostly measured in terms of delta notation (e.g. $\delta^{18}O$). If a radiogenic isotope is involved, then the results are usually expressed as isotopic ratios.

For several decades, radiogenic isotopes strontium (Sr) and lead (Pb) and stable isotopes of light elements (hydrogen (H), carbon (C), nitrogen (N), oxygen (O), sulphur (S)) were the main isotopic systems studied in human remains (Fig. 1). Detection of natural stable isotope abundances for elements of masses greater than 40 amu was very difficult until recently. Two decades ago, the development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and thermal ionization mass spectrometry (TIMS) methods made the measurements of natural stable isotopic ratios for elements up to uranium easier (e.g. Ca: Skulan et al. 1997 (TIMS); Halicz et al. 1999 (ICP-MS); copper (Cu) and zinc (Zn): Maréchal et al. 1999 (ICP-MS); iron (Fe): Walczyk 1997; Beard and Johnson 1999; Johnson and Beard 1999 (TIMS); Belshaw et al. 2000 (ICP-MS); magnesium (Mg): Richter et al. 1999 (TIMS); Galy et al. 2001 (ICP-MS)). These newly measured isotopes have been collectively referred to as "non-traditional stable isotopes" (Albarède and Beard 2004; Anbar and Rouxel 2007; Weiss et al. 2008).

Isotopic fractionation can occur during chemical or physical incomplete element transfer (Bigeleisen 1965; Albarède 2015). Isotopic fractionation is generally mass-dependent, particularly in living organisms, and has been observed for decades in the lighter elements such as C, N and S (DeNiro and Epstein 1978, 1981; McConnaughey and McRoy 1979; Schoeninger and DeNiro 1984; Kelly 2000; Richards et al.

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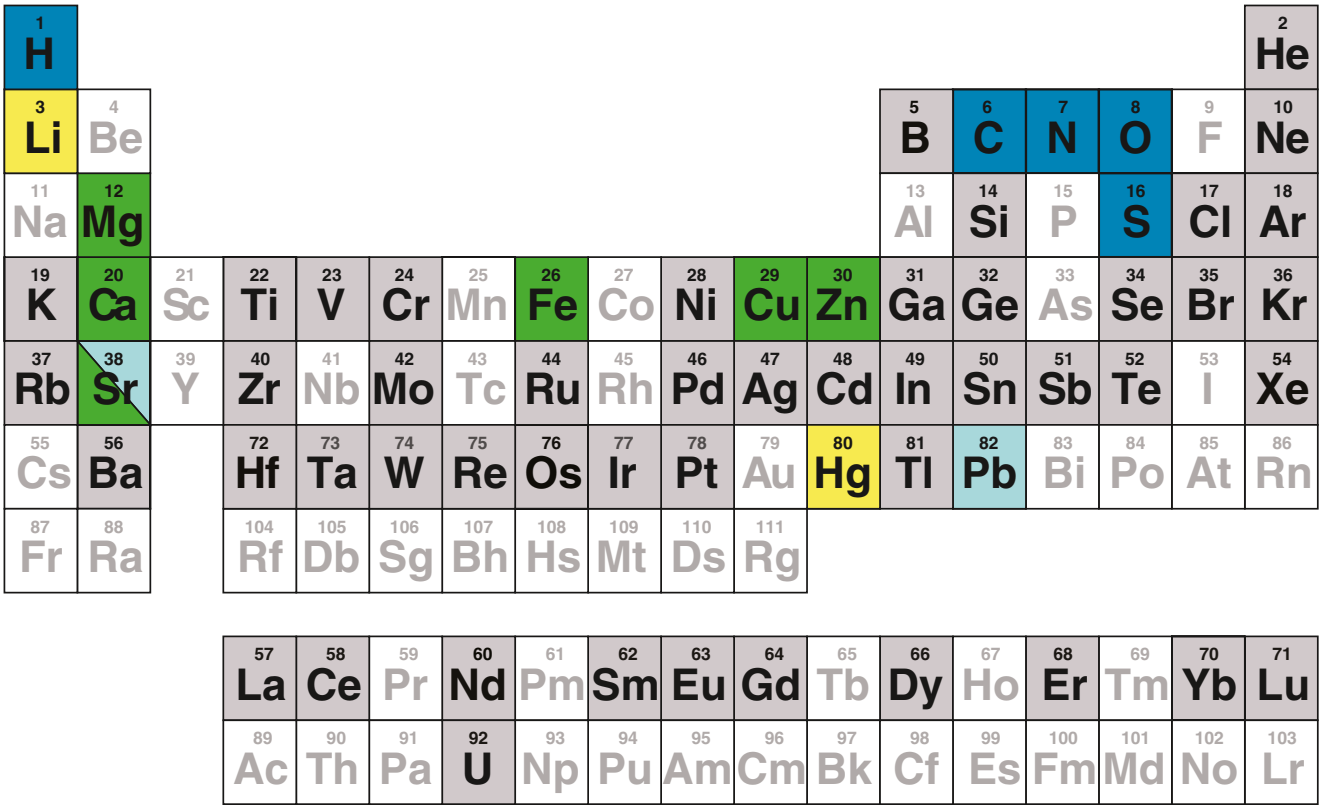

Fig. 1 Periodic table of the elements presenting traditional and non-traditional isotope compositions. *Blue*: Traditional stable isotopes including radiogenic ones (*light blue*). *Green*: Non-traditional isotopes that have been analysed in human remains. *Yellow*: Non-traditional isotopes that have been analysed in animal tissues. *Grey*: Non-traditional isotopes (including radiogenic isotopes) that have at least two stable isotopes

2001). Heavy isotopes of an element tend to have a higher affinity for the compounds where the element can form stiff bonds (Schauble 2004).

"Traditional" stable and radiogenic isotope studies in archaeology

Since the 1970s, isotopic tracers have been frequently used for dietary reconstructions (e.g. Vogel and Van der Merwe 1977; Van der Merwe and Vogel 1978, DeNiro and Epstein 1978, 1981). Historically, most studies on diet have relied on C and N isotopes in bone collagen. These isotopes can trace the consumption of meat, marine foods and C4 plants (maize, sorghum, millet) (Schoeninger and Moore 1992). Compared to sources of information on past diets such as zooarchaeology, organic residues, dental wear or dental calculus (e.g. Grayson 1984; Ryan and Johanson 1989; Dudd et al. 1999; Henry and Piperno 2008), these isotope systems provide a more quantitative approach on the food types eaten at the individual scale, as opposed to the population scale. The use of these isotopes has therefore been incredibly helpful for characterizing the diets and the social organization of our ancestors. However, the major downside of this technique is that it is time-limited: the collagen is not preserved for ancient sites (>100,000 years), or even for much younger sites, depending on the environmental context (Pestle and Colvard 2012). Therefore, information on meat and marine food consumption of ancient hominins is very difficult to retrieve. Carbon isotope studies on dental enamel provide useful information on the type of plants eaten by early hominins or their preys (Sponheimer and Lee-Thorp 1999; Sponheimer et al. 2006; Ungar and Sponheimer 2011) but fail documenting their trophic level. Some laser ablation trace element studies carried out on dental enamel have provided information for older specimens (Sponheimer et al. 2005; Balter and Simon 2006; Balter et al. 2012) but only allow assessment to the nearest trophic level and are highly dependent on the geology.

Oxygen isotopes can be analysed in bioapatite and mostly reflect the isotope composition of drinking water, which is in turn linked to the latitude and climate (Dansgaard 1964; Longinelli 1984; Evans et al. 2006). Consequently, these isotopes can be used for paleoenvironmental or mobility studies (e.g. White et al. 1998; Evans et al. 2006; Touzeau et al. 2013) but can also trace the dietary patterns of animals that primarily source

their water from plants rather than free drinking water (Lee-Thorp and Sponheimer 2006). Hydrogen isotopes can provide similar information using various body tissues (Sharp et al. 2003; Fraser and Meier-Augenstein 2007; O'Brien and Wooller 2007; Ehleringer et al. 2008) but do not allow human provenance to be traced using bioapatite (Holobinko et al. 2011). Sulphur is also commonly used since recent analytical developments now require a smaller amount of collagen to perform S isotope analysis. Sulphur enters local food webs through atmospheric deposition, microbial processes active in soils and local bedrock. As sea spray has a very specific isotope signature, the $\delta^{34}S$ values can indicate coastal living environments (Richards et al. 2001; Richards et al. 2003; Zazzo et al. 2011; Nehlich 2015). As opposed to these light elements, heavier isotopes such as Sr and Pb are not easily fractionated during biological processes: the heavier the element of interest, the smaller the fractionation (Beard and Johnson 1999). A few decades ago, the same isotopic ratio was expected for heavy elements from the soil to the top of a trophic chain, in all organs and tissues (Gosz et al. 1983). With the recent improvement in mass spectrometry, this expectation has since been invalidated for a number of non-traditional isotopic systems: first for Fe isotopes (Beard and Johnson 1999) and recently for a much heavier element, mercury (Laffont et al. 2009, 2011). However, the heavy element isotopic system investigated in "traditional" archaeological studies is radiogenic strontium ($^{87}Sr/^{86}Sr$). The classical analytical procedure for the measurement of this ratio would erase any small biological fractionation, if present (Gosz et al. 1983). Indeed, for Sr, all reported $^{87}Sr/^{86}Sr$ ratios are corrected for fractionation according to the measured deviation of the $^{86}Sr/^{88}Sr$ ratio in order to correct the instrumental fractionation mass bias (Gosz et al. 1983). As biological fractionation is mass-dependent, this protocol erases these small isotopic differences. This also applies to radiogenic lead (e.g. $^{206}Pb/^{204}Pb$), a system also used in bioarchaeological studies (e.g. Montgomery et al. 2000; Chiaradia et al. 2003; Turner et al. 2009). As a consequence, Sr and Pb radiogenic isotope compositions of human tissues reflect that of the soil where a living organism gets its food (animals or plants) (Bentley 2006). These isotope compositions are therefore frequently used to trace the mobility of past populations (e.g. Copeland et al. 2008; Richards et al. 2008; Copeland et al. 2011; Balter et al. 2012). Concentrations of radiogenic elements such as Sr and Pb increase over time. However, this increase does not matter for archaeology or biomedical studies because daughter isotope production is implemented beyond the timescale of interest or the lifetime of a living organism: the half-life of ^{87}Rb is $t_{1/2} = 4923 \times 10^{10}$ years and the radionuclides involved in the U-Th series, which produce Pb isotopes, have half-lives ranging from 10^8 to 10^{10} years.

Potential of "non-traditional" isotopes for archaeology

As for traditional isotopes, the measurements of non-traditional isotope ratios have been developed by geochemists. While it was rarely undertaken at first, this type of analysis has become a discipline per se within the last 10 years (Albarède and Beard 2004; Anbar and Rouxel 2007). Initially, non-traditional stable isotope studies in biological materials have been mostly carried out on plants (e.g. Weiss et al. 2005; Guelke and von Blanckenburg 2007; Viers et al. 2007; Black et al. 2008; Moynier et al. 2009; von Blanckenburg et al. 2009; Aucour et al. 2011; Weinstein et al. 2011; Jouvin et al. 2012; Hindshaw et al. 2013) and human or animal tissues (e.g. Skulan and DePaolo 1999; Walczyk and von Blanckenburg 2002; Ohno et al. 2004; Ohno et al. 2005; Balter et al. 2010; Albarède et al. 2011; Balter et al. 2013; Sampson et al. 2013; Moynier et al. 2013; von Blanckenburg et al. 2014). They are now applied to biomedicine (e.g. Albarède et al. 2011; Morgan et al. 2011, 2012; Lauwens et al. 2016), archaeological artefacts (e.g. Desaulty et al. 2011; Albarède et al. 2012; Balliana et al. 2013; Delile et al. 2014; Baron and Coustures 2015) and human remains, which will be discussed throughout this review.

In order to apply the study of an isotopic system to the field of anthropology, the following two criteria must be met: (1) the selected element needs at least two stable isotopes, and (2) its isotope concentration in human organs or tissues needs to be above the detection limit of the mass spectrometer. Additionally, the isotope analyses of the element of interest first require the development of an extraction and purification protocol, as well as a minimum sample size to perform measurements for archaeological applications. A list of candidate elements is given in Fig. 1. At this time, only seven elements have been investigated for their isotopic composition in the human body: calcium (Ca), Cu, Fe, Mg, mercury (Hg), Sr (stable isotopes) and Zn (Fig. 1). Copper, Fe and Zn isotopes are often studied together as they can be isolated using the same chemical purification protocol (Maréchal et al. 1999). Zinc data are the most abundant for several reasons: (1) Zn concentration is higher than that of Cu in body organs and tissues; (2) Zn isotopic measurements require less advanced technology relative to Fe isotopes; and (3) the chemical purification of Zn alone (Moynier et al. 2006) is cheaper and less time-consuming.

Natural isotopic abundances of the abovementioned elements and their associated delta notation are given in Table 1. Three factors are likely to trigger isotopic variability within the human body:

Table 1 Abundances of stable isotopes for elements studied for their non-traditional isotope compositions

Element	Symbol	Group	Abundances	Delta notation	Radiogenic ratio
Calcium	Ca	Alkaline earth metal	$^{40}Ca^{a}$ (96.9 %), ^{42}Ca (0.6 %), ^{43}Ca (0.1 %), ^{44}Ca (2.1 %), $^{46}Ca^{a}$ (0.004 %), $^{48}Ca^{a}$ (0.2 %)	$\delta^{44/42}Ca$ (ICP-MS) $\delta^{44/40}Ca$ (TIMS)	
Copper	Cu	Transition metal	^{63}Cu (69.2 %), ^{65}Cu (30.9 %)	$\delta^{65}Cu$	
Iron	Fe	Transition metal	^{54}Fe (5.8 %), ^{56}Fe (91.7 %), ^{57}Fe (2.2 %) and ^{58}Fe (0.3 %)	$\delta^{56}Fe$, $\delta^{57}Fe$	
Magnesium	Mg	Alkaline earth metal	^{24}Mg (79.0 %), ^{25}Mg (10.0 %), ^{26}Mg (11.0 %)	$\delta^{25}Mg$, $\delta^{26}Mg$	
Strontium	Sr	Alkaline earth metal	^{84}Sr (0.6 %), ^{86}Sr (9.9 %), ^{87}Sr (7.0 %), ^{88}Sr (82.6 %)	$\delta^{88}Sr$	$^{87/86}Sr$
Zinc	Zn	Transition metal	$^{64}Zn^{a}$ (49.2 %), ^{66}Zn (27.7 %), ^{67}Zn (4.0 %), ^{68}Zn (18.5 %), $^{70}Zn^{a}$ (0.6 %)	$\delta^{66}Zn$, $\delta^{67}Zn$, $\delta^{68}Zn$	

[a] Isotopes that are observed stable but actually radioactive

(1) *Diet*: isotopic fractionation can occur during intestinal absorption or excretion, inducing isotopic differences between the body isotopic compositions of a prey animal and its predator. Predator–prey isotopic differences can be observed for instance in the case of N isotopes (Fig. 2). Significant isotopic differences between food categories belonging to the same trophic level can also exist, and the consumption of these different food categories can therefore be traced (e.g. ^{13}C isotope compositions of C_3/C_4 plants). (2) *Environmental context*: like the radiogenic ratio of Sr ($^{87}Sr/^{86}Sr$), isotope composition of the soil can impact that of the whole food web. (3) *Metabolism:* metabolic reactions within the body can also generate isotope fractionation. Metabolic processes such as disease could therefore be traced. This is particularly true for non-traditional isotopes: unlike traditional ones, they do not belong to the CHNOPS[1] (Fig. 1), that is to say the most common elements in living organisms. They are therefore more likely to trace specific metabolic processes, being involved in less biological reactions. When a dietary, environmental or metabolic process triggers major isotope variability of one element, its isotope composition can be used to trace the process of interest (Fig. 2). As a consequence, isotope studies carried out on human tissues can help reconstruct the diet, mobility and health conditions of past populations.

In this review, we will assess the natural distribution of these isotopic systems in food webs and their established or potential contribution for bioarchaeological studies. We will show that they can be used alongside Sr radiogenic ratios and light stable isotopes for palaeodiet, weaning and mobility tracing, but we will also discuss how they could be used to investigate other processes, such as biological sex or age at menopause. Often, the studies reported in this review offer only preliminary conclusions but constitute pioneer research: even if non-traditional stable isotope studies are still in their infancy, their potential as promising new archaeological tools has already been shown.

[1] CHNOPS stands for carbon hydrogen, nitrogen, oxygen, phosphorus and sulphur

Material and methods in non-traditional isotope studies

Material

Material candidates for non-traditional isotope analyses

All of the non-traditional isotope systems investigated in human remains have been established in bioapatite, a calcium phosphate ($Ca_{10}(PO_4)_6(OH)_2$) located in dental enamel and tooth dentine as well as in the mineral part of bones. Besides the classic isotope measurements of O, Ca isotope compositions can also be measured (Firestone and Shirley 1998). Phosphorus, having only one stable isotope, does not meet the criteria for isotope studies (Fig. 1). Amongst the minor elements, Mg isotope compositions have been described in bone and teeth (Martin et al. 2014, 2015b). Magnesium substitutes to Ca in the bioapatite lattice. This substitution mechanism also applies to several trace elements such as Zn and Sr (Gross and Berndt 2002). The incorporation process of Fe and Cu in bioapatite is unclear but could also be a substitution to Ca atoms. Iron and Zn isotopes have also been measured in human hair, with a minimum amount of 100 mg required for one measurement (Stenberg et al. 2004; Ohno et al. 2005). The mass required for analyses first depends on the concentration of the element of interest in the chosen archaeological material. At a smaller but still important scale, it is also a function of the mass spectrometer used for the isotopic measurements, the isotopes that can be analysed, as well as their abundances. These masses are summarized in Table 2. Depending on the material chosen for analysis, the isotopic signal will represent different periods of the life of past individuals. Bones are renewed throughout life while dental enamel and dentine do not change after their formation. Dental tissues therefore record the isotopic signature of childhood, and bones average the last 5 to 20 years of life (Pate 1994; Sealy et al. 1995; Hedges et al. 2007). Independent of this temporal difference, bone and dental enamel do not exhibit the same isotope composition, whatever the element

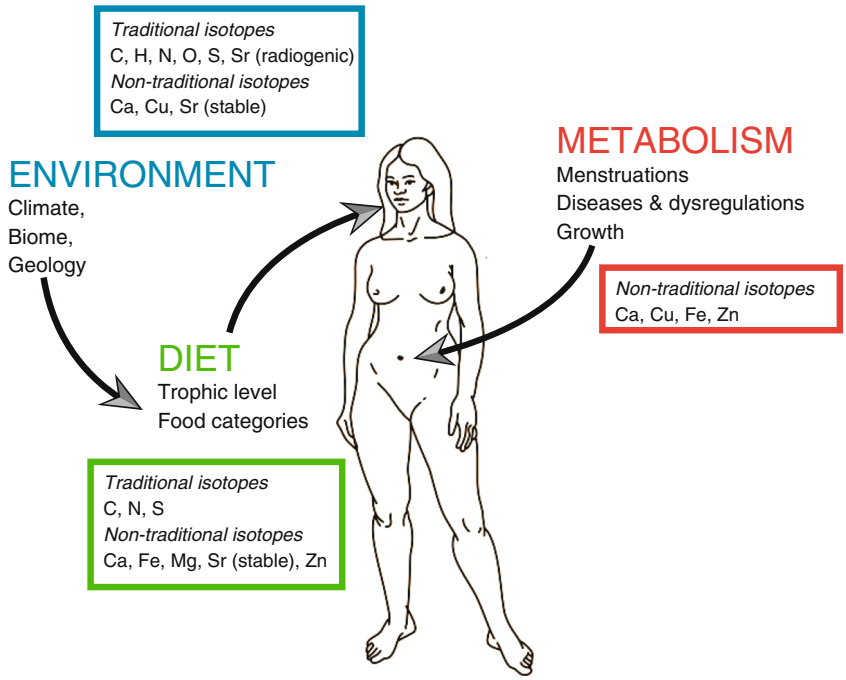

Fig. 2 The woman template originates from the pioneer plaque (NASA, no copyright). Factors influencing traditional and non-traditional isotope compositions of different elements of the human body

considered. Offsets between bone and dental enamel isotopic values have been reported for all the elements in which isotopic compositions have been measured in these two tissues (C and O (Warinner and Tuross 2009), Ca (Heuser et al. 2011), Mg (Martin et al. 2014), Zn (Jaouen et al. 2016a)), though never really explained.

Diagenesis

When choosing a material for non-traditional isotope analyses, careful attention has to be paid to potential soil contamination. Bone and dentine are more porous than dental enamel and are therefore more likely to incorporate elements from aqueous fluids circulating in soils (Reynard and Balter 2014). This problem is obviously more relevant for trace elements: it has been shown that diagenesis of archaeological bones is not likely to overprint the biogenic signature of Ca isotopes (Reynard et al. 2010), even though it might happen for very old bones such as those of dinosaurs (Heuser et al. 2011). On the other hand, some elements such as Fe are present as traces in human remains (~100 ppm) but show very high concentrations in soil (1 to 40 %). Depending on the environmental context, historical bones can incorporate high levels of diagenetic Fe, which will overprint the isotopic composition of interest (Kohn et al. 1999; Martínez-García et al. 2005). Several tests have been described in the literature to investigate bone diagenesis: collagen preservation, REE content, crystallinity index, Ca/P ratios, etc. (Price et al. 1992; Hedges 2002; Beasley et al. 2014; Reynard and Balter 2014). However, it has been shown that these tests trace different diagenetic processes that are not necessarily related (Trueman et al. 2008). Recrystallization can occur in a bone with preserved trace element content, but geochemical perturbations can also happen without detectable change of crystallinity (Pucéat et al. 2004). To overcome this problem, Reynard and Balter (2014) suggested using a diagenetic test involving the trace element of interest. This test consists of assessing if the trace element isotopic compositions of various samples from a site are correlated to their concentrations, which is expected if these samples incorporated various proportions of a diagenetic component (Albarède 1996). Dental enamel is generally considered much more preserved because of a higher degree of mineralization and low porosity (Lee-Thorp and van der Merwe 1991; Wang and Cerling 1994; Hoppe et al. 2003; Lee-Thorp and Sponheimer 2003). It is considered a material of choice for trace element analyses. However, depending on the age and the environmental context of the sample, diagenesis can affect the integrity of biogenic signatures in dental enamel (Kohn et al. 1999; Schoeninger et al. 2003) and should be assessed.

Methods

Sample preparation

Most of the non-traditional isotope systems' elements are present in minor or trace concentrations in teeth and bones. Therefore, their analyses using mass spectrometry require the removal of the matrix, in order to avoid isobaric interferences with isotopes of other elements or molecules of the same mass.

Table 2 Summary of factors influencing non-traditional isotope compositions and material required for analyses

Element	Amount in bioapatite	Trophic level effect	Other dietary factors	Geographical factor	Metabolic factors	Measurement methods	Sampled material	Material of analyses
Ca	Major element	Yes	Bone consumption, dairy products?	Yes, important in terrestrial environments	Bone loss	TIMS, MC-ICP-MS, laser ablation	40 µg	Bone, teeth
Cu	Trace element	Unclear	Unknown	Yes, important	Menstruations, cancer, Wilson disease	MC-ICP-MS	75 mg	Dental enamel, non-diagenetic bones
Fe	Trace element	Yes	Plants from strategy I and II?	Never observed	Menstruations, hemochromatosis	MC-ICP-MS	50 mg	Dental enamel, non-diagenetic bones
Mg	Minor element	Yes	Meat consumption	Yes	Unknown	MC-ICP-MS	1 mg	Dental enamel, non-diagenetic bones
Sr	Trace element	Yes	Bone consumption	Yes, very important	Unknown	MC-ICP-MS	20 mg	Dental enamel, non-diagenetic bones
Zn	Trace element	Yes	Meat, bone consumption High trophic level fish?	Slight	Cancer	MC-ICP-MS	20 mg	Dental enamel, non-diagenetic bones

For example, a molecule made of the major isotopes of Ca and O (^{40}Ca and ^{16}O) is likely to interfere with one of the Fe isotopes (^{56}Fe), inducing a bias in the measurement of the δ^{56}Fe values. This purification step is achieved using chromatography on columns. If the element of interest is a major element, the purification step will not be mandatory, as shown in blood by Anoshkina et al. (2015) for Fe isotopes. However, in the case of Ca, which represents almost one atom out of two in bioapatite, the removal of the matrix is required to avoid destabilization of the plasma due to the presence of phosphorus. The protocols used for Ca, Fe, Cu and Zn purifications prior to isotopic analyses have recently been summarized by Costas-Rodriguez et al. (2016). The purification of Mg has been described by Martin et al. (2014), whereas the technique employed for stable isotope compositions of Sr remains unpublished. The purification protocol used for the radiogenic ratio of strontium (^{87}Sr/^{86}Sr) is not quantitative and cannot be used for δ^{88}Sr assessments (Hartman and Richards 2014). Incomplete recovery of an element during ion exchange resin chromatography on columns triggers significant isotopic fractionation on non-radiogenic stable isotope ratios (Maréchal et al. 1999).

Isotopic analyses

Isotopic ratios of trace elements are measured using TIMS or MC-ICP-MS. The main difference between these two instruments consists of how the sample is introduced and ionized, but the analytical aspect of these techniques is similar. The TIMS measurements are usually more precise but also time-consuming. Most of the non-traditional isotopes are analysed using MC-ICP-MS (Costas-Rodríguez et al. 2016, Table 2), with the exception of Ca isotopes that are analysed using either technique (e.g. Skulan and DePaolo 1999; Heuser and Eisenhauer 2010; Reynard et al. 2010; Tacail et al. 2014). In the case of MC-ICP-MS instrumentation, the ratio measured will be ^{44}Ca/^{42}Ca, instead of the ^{44}Ca/^{40}Ca ratio. This technique uses argon as a carrier gas, which interferes with the isotope ^{40}Ca. Stable isotope fractionation is mass-dependent, which implies that $\delta^{44/42}\mathrm{Ca} = \delta^{44/40}\mathrm{Ca} \times \frac{\left({}^{1}/_{m_{42}} - {}^{1}/_{m_{44}}\right)}{\left({}^{1}/_{m_{40}} - {}^{1}/_{m_{44}}\right)}$, that is too say $\delta^{44/42}\mathrm{Ca} = 0.4773 \times \delta^{44/40}\mathrm{Ca}$ (Young et al. 2002; Sime et al. 2007). Details on non-traditional isotope measurements have been described by Albarède and Beard (2004).

Recent studies demonstrated the possibility of measuring non-traditional isotope compositions of human tissues using laser ablation. Protocols for Ca isotope laser analyses were recently developed for biological or synthetic apatite (Tacail et al. 2016; Li et al. 2016). Isotopic measurements of other elements may be more difficult to achieve because of the low abundance of Fe, Zn, Cu or Mg in bioapatite but not impossible as shown by Resano et al. (2013), who measured the Cu isotopic composition of dried urine pellets.

Diet and non-traditional isotope compositions

Two dietary factors are likely to impact isotopic compositions of human bodies: (1) the actual isotopic compositions of food products and (2) the fractionation occurring during intestinal absorption, which can be influenced by the atomic environment of the element of interest and, therefore, the food category. For instance, the precipitation of Zn with phytates contained in plants, which happens within the intestinal tract, seems to be isotopically selective towards light isotopes (Jaouen et al. 2013b). The consumption of plants is therefore associated with an enrichment of the consumer tissues in Zn heavy isotopes, which are more bioavailable[2]. In the case of animal product consumption, there is no evidence of an existing process influencing the bioavailability[2] of one isotope over another and no fractionation apparently occurs during intestinal absorption (Jaouen et al. 2013b). Another illustration of these two dietary factors can be given by the carbon isotope compositions of food products. Marine fish tissues and C_3 plants generally exhibit a discrepancy of ≈15 ‰, whereas the isotope fractionation during intestinal absorption is approximately 0 to 2 ‰ for the two food categories (Bocherens and Drucker 2003). As a consequence, the actual isotope composition of food products is the main factor of C isotope variations in the human body. In the case of N isotopes, an isotope fractionation of 3 to 5 ‰ between the bone collagen and the food product can be observed, and this significant increase can therefore be used as an indicator of the trophic level (Hedges and Reynard 2007). An important step for the calibration of new dietary tracers is the investigation of the existence of a trophic level effect, as well as the identification of food categories with a specific isotope composition.

Trophic level effect

The existence of a trophic level effect has been demonstrated for most of the non-traditional isotopic systems studied so far: Ca (Clementz et al. 2003; DePaolo 2004; Heuser et al. 2011; Martin et al. 2015a), Mg (Martin et al. 2014; Martin et al. 2015b), Sr (Knudson et al. 2010; Tütken et al. 2015), Zn (Van Heghe et al. 2012; Costas-Rodríguez et al. 2014; Jaouen et al. 2016a, 2016b) and Fe (Walczyk and von Blanckenburg 2002; Walczyk and von Blanckenburg 2005; Jaouen et al. 2013b; von Blanckenburg et al. 2013). For Ca, this pattern is not systematically observed (Melin et al. 2014). This trophic level effect can correspond to an enrichment in light isotopes through the trophic chain (like for C and N isotopes) or a depletion. Enrichment in light isotopes can also be observed for elements such as Ca, Fe and Sr but not for Mg, Cu and Zn (Fig. 3, Tütken et al. 2015). The case of Zn is very peculiar: as mentioned before, a plant-based diet seems to trigger the preferential intestinal absorption of Zn heavy isotopes, whereas no fractionation is expected in a meat-based diet, due to a quantitative absorption of the element (Lönnerdal 2000; Jaouen et al. 2016a, 2016b). However, because animal muscles are depleted in heavy Zn isotopes compared to the bulk isotope composition of the body, body tissues of meat consumers have lower isotope compositions than those of their prey (Jaouen et al. 2016a, 2016b, Fig. 3). Similarly, von Blanckenburg et al. (2013) have shown that vegetarian diets are associated with a Fe isotopic fractionation factor 1.5 times higher than that of omnivore diets, but in this case, the light isotopes are preferentially absorbed. Because the Fe isotope composition of vegetarians' diet is generally much higher than that of omnivores, the blood isotope compositions of these two groups are similar and cannot be distinguished (Van Heghe et al. 2012; von Blanckenburg et al. 2013). It should be noted that ovo-lacto-vegetarian and omnivore diets both mix animal and plant products. The difference reported between herbivore and carnivore Fe isotope compositions could therefore be due to pure meat and plant-based diets. Mercury isotopes, a system not yet investigated in archaeological materials, also show a preferential selection for light isotopes by living organisms. Laffont et al. (2009) reported enrichment of 0.5 ‰ relative to the atomic mass when comparing δ^{202}Hg values between fish and humans, and Gehrke et al. (2011) observed an enrichment of about 0.6 ‰ between fish and sediments (which contain the primary source of dietary Hg). As expected, the range of fractionation within a trophic chain is about 10 times smaller for alkaline earth and transition metals than for lighter elements like nitrogen and carbon isotopes (Fig. 3).

Traceability of food categories

Plant consumption

The existence of isotope variability amongst plants has been documented for Ca (von Blanckenburg et al. 2009; Hindshaw et al. 2013), Cu (Weinstein et al. 2011; Jouvin et al. 2012), Fe (Guelke and von Blanckenburg 2007; von Blanckenburg et al. 2009), Mg (Black et al. 2008) and Zn (Weiss et al. 2005; Viers et al. 2007; Moynier et al. 2009; Aucour et al. 2011; Jouvin et al. 2012). Isotopic fractionation occurs within a plant, leading to different isotopic compositions between the roots, stems and leaves. Therefore, we can expect isotopic differences between browsers (which have a leaf-based diet) and grazers (which mostly feed on grasses). So far, this difference has been observed for Mg (Martin et al. 2015b) and Zn isotopes (Jaouen et al. 2016a). Significant differences have also been observed in the Fe isotope composition of plants

[2] Bioavaibility is potential absorption of a chemical species as a function of external factors such as the food matrix and the chemical form of the element in question.

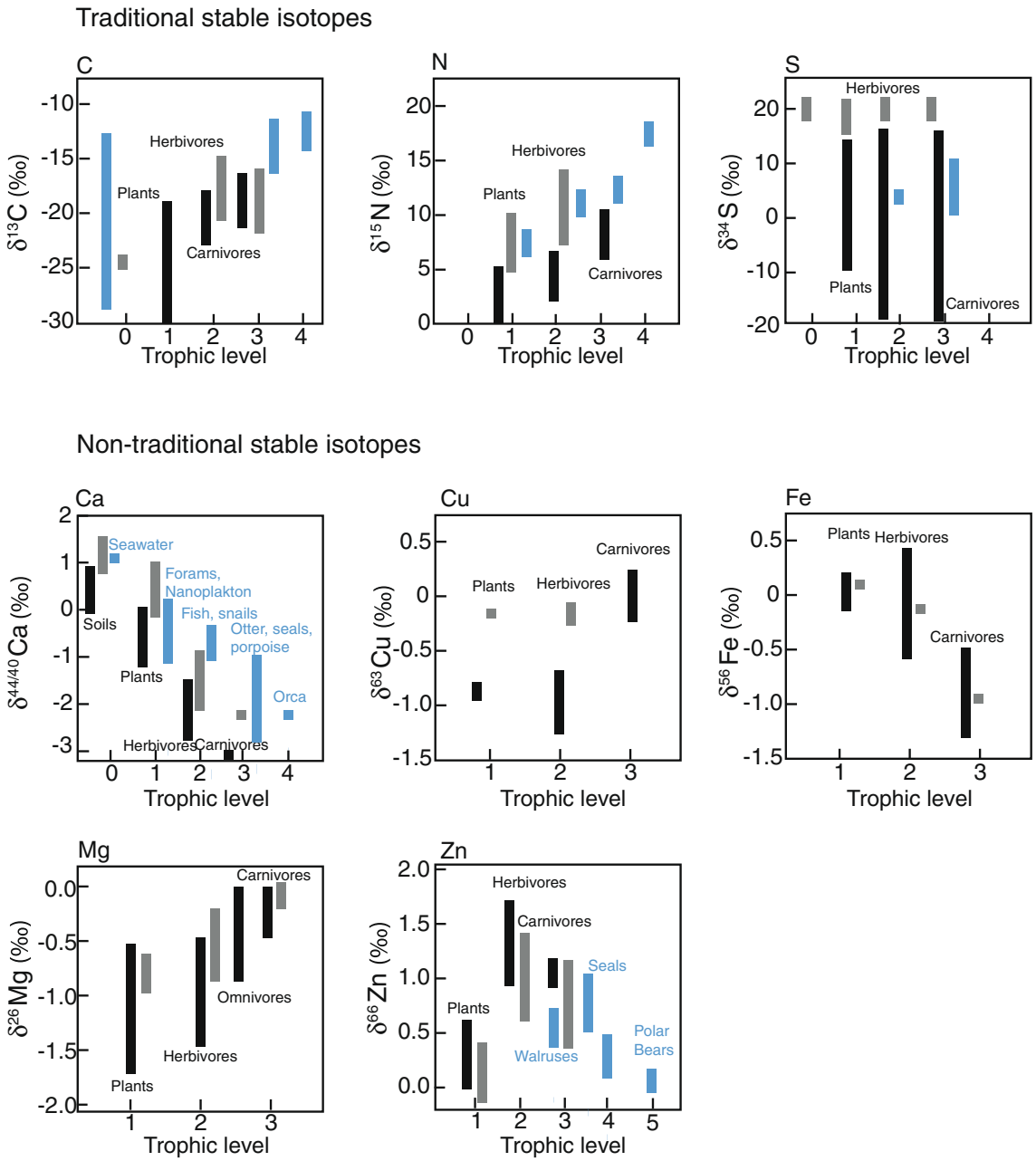

Fig. 3 Trophic level effect on classic and non-traditional isotope compositions. *Blue colours* correspond to a marine environment. *Black and grey* correspond to two different terrestrial food webs. After McConnaughey and McRoy (1979) and Schoeninger and DeNiro (1984) (C isotopes), Minagawa and Wada (1984), Kelly (2000) and Schoeninger and DeNiro (1984) (N isotopes), Nehlich (2015) (S isotopes), Skulan and DePaolo (1999), Clementz et al. (2003) and DePaolo (2004) (Ca isotopes) and Jaouen et al. (2013a, 2016a, 2016b) (Cu, Fe and Zn isotopes) and Martin et al. (2014, 2015b) (Mg isotopes)

using a different strategy for Fe mobilization and uptake from the soils (Guelke and von Blanckenburg 2007). This strategy is confined to grasses, whereas the preceding strategy is used by all other types of plants (Marschner and Römheld 1994). The plants using the first strategy, such as vegetables, usually show lower δ^{56}Fe values relative to plants using the second strategy, such as crops. The Fe isotopic signature of the consumption of only one of these two plant types has yet been investigated.

Bone consumption

Isotopic compositions of body tissues are highly variable within an organism (Skulan and DePaolo 1999; Walczyk and von Blanckenburg 2005; Balter et al. 2010; Balter et al. 2013; Moynier et al. 2013; Balter and Vigier 2014). Consequently, the consumption of specific organs or tissues could impact the isotopic signature of carnivore body tissues. Bones are enriched in Zn heavy isotopes and Ca light isotopes

relative to muscles. It seems that the bone consumption occurring in some carnivore species, such as hyenas, impacts the isotopic signature of their bones and teeth, making them distinguishable from pure meat-feeders (Tütken et al. 2015; Jaouen et al. 2016a). However, these recent findings need further investigation to be confirmed.

Dairy consumption

Most dietary Ca comes from dairy products and vegetables, so meat and water can be considered negligible sources (Chu et al. 2006; Heuser and Eisenhauer 2010). In 2006, Chu et al. (2006) analysed herbivore milk and discovered very low $\delta^{44/42}$Ca values, depleted by about 0.5 ‰ relative to the diet of these animals. They also analysed dairy products such as curd and whey and showed that fermentation processes do not induce significant isotopic fractionation. They suggested that Ca isotopes could be used to trace dairy product consumption. Reynard et al. (2011) tested this hypothesis by comparing bones from Epipalaeolithic and Mesolithic sites, where dairy consumption is unlikely, to bones from a medieval site. They systematically observed an enrichment of human bones in light Ca isotopes compared to the faunal bones, but the range of fractionation was the same for each site (0.2–0.4 ‰, Reynard et al. 2011). As a result, the trophic level effect seems to overprint the isotope signature of dairy product consumption.

Breastfeeding and weaning

The relationship between the breastfed child and the mother is similar to the prey–predator relationship from a dietary point of view. The trophic level of the child is higher than that of the mother until weaning. Following this idea, numerous studies investigate the breastfeeding duration in archaeological populations using light stable isotopes, mostly δ^{15}N values (Richards et al. 2002; Fuller et al. 2006; Herrscher 2013), but also with δ^{13}C and δ^{34}S (Wright and Schwarcz 1998; Richards et al. 2002; Nehlich et al. 2011). These analyses are carried out on bone proteins, which are not always preserved. As a consequence, major elements contained in the mineral phase are of great concern for weaning pattern assessment. Attempts have been performed using O isotopes on dental enamel carbonates but provided contradictory results (Wright and Schwarcz 1998; Williams et al. 2005; Herrscher 2013). Non-traditional isotopes could therefore be of interest for weaning age assessment. As mentioned before, milk also has low $\delta^{44/42}$Ca values. Human milk is no exception as it corresponds to the lowest ^{44}Ca/^{42}Ca ratios measured in biological material alongside bones (Chu et al. 2006; Reynard et al. 2010). It has therefore been suggested that Ca isotopes could be used as weaning indicators (Chu et al. 2006). Reynard et al. (2013) tested this assumption using human archaeological populations from the Turkish Neolithic site Aşıklı Höyük and skeletons from Christ Church, Spitalfields, buried during the eighteenth century. At Aşıklı Höyük, Ca isotope ratios in milk-consuming infants and juveniles were lower than those of adults, as expected. Also, $\delta^{44/42}$Ca correlates to δ^{15}N values. However, at Spitalfields, no significant differences between age group and no correlation with traditional stable isotopes have been observed (Reynard et al. 2013). Wright (2014) observed a weaning pattern in sheep tooth enamel by comparing the Ca isotope compositions of modern teeth formed successively during their infancy. These contradicting results remain unexplained. More work is needed to understand the impact of diet and metabolism on Ca isotopes in the human body, in order to fully recognize their potential for archaeological studies. Some efforts have however already been made by combining isotope analyses with box models (Skulan and DePaolo 1999; Heuser and Eisenhauer 2010). The results shed light on the fundamental role of both mineral bone balance and Rayleigh type Ca isotope fractionation in the kidneys on Ca isotope compositions of body tissues.

Environmental context and non-traditional isotope compositions

Assessing the interpopulation variability is a crucial step in non-traditional isotope studies in a bioarchaeological perspective. High variability between different sites opens up possibilities for developing mobility proxies. Two factors are likely to generate isotopic variations in soils: (1) the local geology and (2) environmental processes related to the vegetation, water circulation and climate.

Differences between the isotopic composition of animal or human remains coming from different locations have been documented for Ca (Reynard et al. 2010), Cu (Jaouen et al. 2013b), Mg (Martin et al. 2014) and Sr (stable isotopes, Knudson et al. 2010) (Figs. 3 and 4). On the other hand, Fe isotopic composition of animal and human remains seems to be homogenous wherever the provenance (Jaouen et al. 2013b). This is also true for Fe isotopes in human blood (Jaouen et al. 2013a), with the exception of a Thai female population, which exhibits blood Fe isotope compositions lower than expected (Fig. 4, Hotz and Walczyk 2013). The origin of this difference is unclear. The impact of the environmental context on Zn isotope compositions of a food web is also unclear, albeit suspected (Jaouen et al. 2013b; Jaouen et al. 2016a, 2016b). Consequently, the application of non-traditional analyses for dietary reconstruction will require systematic analyses of the associated fauna or soils.

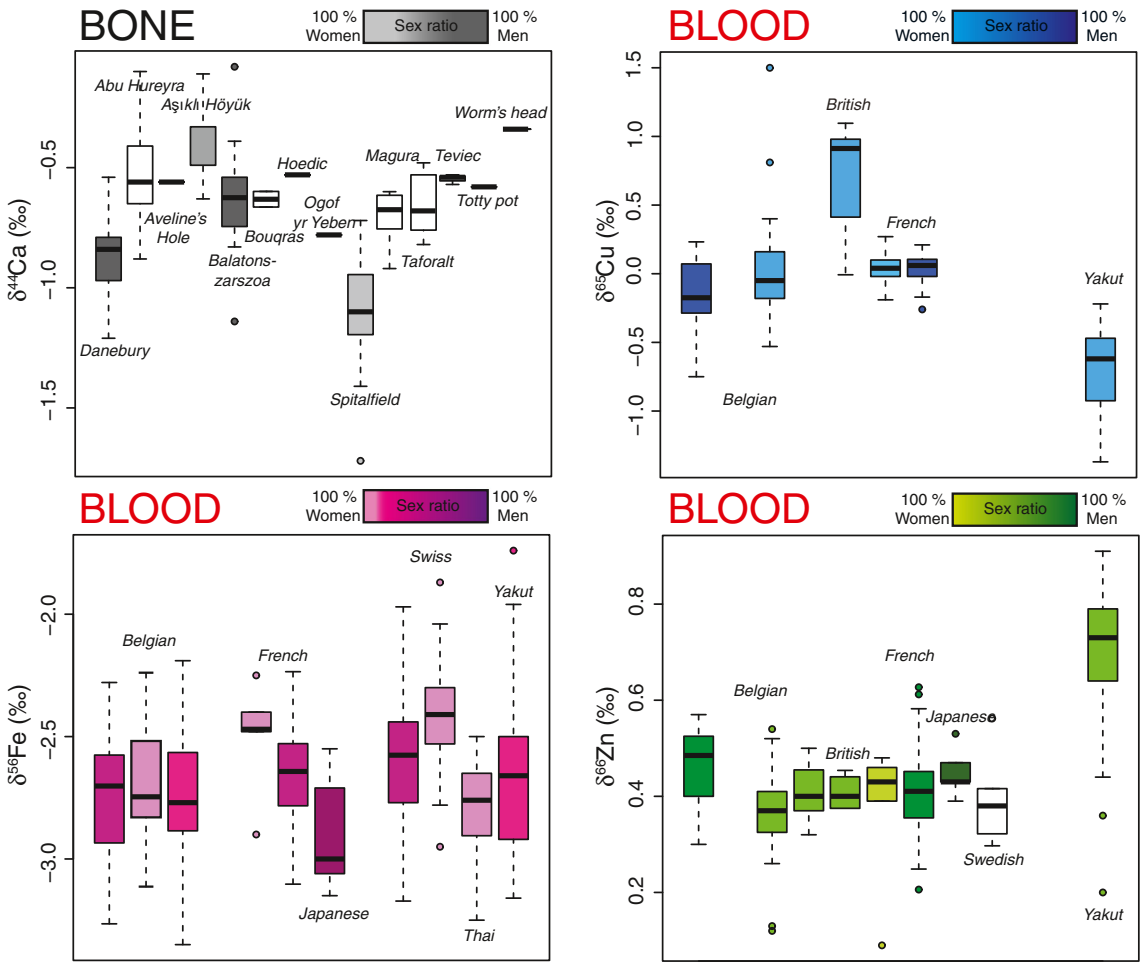

Fig. 4 Range of isotope values observed in bones (for Ca isotopes), whole blood (for Cu, Fe and Zn isotopes) or red blood cells (Fe, Zn isotopes). Data come from Reynard et al. (2011, 2013) (Ca isotopes), Van Heghe et al. (2012, 2014), Larner et al. (2015), Albarède et al. (2011) and Jaouen et al. (2013a) (Cu isotopes), Van Heghe et al. (2012, 2013, 2014), Albarède et al. (2011), Jaouen et al. (2013a), Ohno et al. (2005), Walczyk and von Blanckenburg (2002) and Hotz and Walczyk (2013) (Fe isotopes) and Van Heghe et al. (2012, 2013, 2014), Costas-Rodríguez et al. (2014), Larner et al. (2015), Albarède et al. (2011), Jaouen et al. (2013a), Ohno et al. (2004) and Stenberg et al. (2005) (Zn isotopes). Delta values are expressed relative to NIST 915a, IRMM-014, NIST 976 and JMC-Lyon 3-0749 standards, respectively

Metabolism and non-traditional isotope compositions

Elements with non-traditional isotopic composition can play a central role in human metabolism. Calcium is the main constituent of bones and teeth, and Mg contributes to their mineralization. Both elements play a crucial role in many important physiological functions such as muscular contraction and neurotransmission (Nadler and Rude 1995). Iron and Cu are involved in bone formation and maintenance, electron and oxygen transfer and erythropoiesis amongst other things (Arredondo and Núñez 2005). Zinc is present in more than 300 metalloproteins, most of which have enzymatic or structural properties (Cousins 1985). Being essential nutrients, the concentrations of these elements are finely regulated by the organism, if only to remain in the interval defined by deficiency and toxicity levels. Conversely, isotope abundances a priori do not undergo regulation mechanisms in mammalian bodies. They can therefore provide additional physiological information on elemental metabolism under normal or pathological conditions.

Metabolic dysregulations

Non-traditional isotopes have recently been the subjects of many studies because of their potential to trace metabolic diseases such as hemochromatosis (Krayenbuehl et al. 2005; Stenberg et al. 2005, Walczyk and von Blanckenburg 2005), iron deficiency (Van Heghe et al. 2013), Wilson disease (Aramendía et al. 2013; Resano et al. 2013), cancers (Balter et al. 2015; Larner et al. 2015; Télouk et al. 2015; Bondanese et al. 2016; Chamel et al. 2016) or bone mineral balance (Skulan et al. 2007; Heuser and Eisenhauer 2010; Morgan et al. 2011; Anbar et al. 2013). The potential of these isotopes as a new diagnostic tool in biomedicine has recently been fully described in four reviews (Albarède et al. 2016;

Costas-Rodríguez et al. 2016; Heuser 2016; Larner 2016). Even if it has not yet been investigated, mineralized tissues are likely to record isotopic signatures of these pathologies. Indeed, it has already been shown that they can trace the Fe, Cu and Zn isotopic signatures of sex (Jaouen et al. 2012) and diet (Jaouen et al. 2016a, 2016b), previously observed in blood (Walczyk and von Blanckenburg 2002; Albarède et al. 2011; Costas-Rodríguez et al. 2014). Such identification of diseases would open up a new field in palaeoepidemiology and would have the potential to trace the emergence of specific metabolic diseases.

Sex-dependent isotopic differences

The first study published on Fe isotopes in human blood highlighted different isotopic compositions between men and women (Walczyk and von Blanckenburg 2002). Later, it was shown that these differences also exist for Cu isotopes but not for Zn isotopes (Albarède et al. 2011) and can be seen in human bones (Jaouen et al. 2012). These sex isotope differences could be due to a metabolic response to the menstrual iron losses: the mechanism involved could be the higher Fe intestinal absorption of women, the mobilization of liver Fe stores, which are enriched in heavy Fe isotopes, or a combination of the two (Hotz et al. 2012; Jaouen and Balter 2014). As a consequence, the sex isotope differences disappear after menopause (Jaouen and Balter 2014; Van Heghe et al. 2014), following different timelines on the turnover of the element: a couple of months for Cu and several years for Fe. Surprisingly, the study of a Yakut population showed no differences between pre- and post-menopausal women for Fe and the opposite trend for Cu compared to European populations (Jaouen et al. 2013a). This unique observation remains unexplained. Interestingly, an isotopic difference between sexes has also been highlighted for Ca isotopes in sheep bones (Reynard et al. 2010). The explanation is that the females suckled their lambs, thus altering their Ca bone balance. This pattern was also observed in human bones, though it was not significant. Besides, the number of times a woman has given birth is not correlated to the Ca isotope composition of her bones (Reynard et al. 2013). Further investigations did not confirm this trend, but the sex ratios of the studied populations were often imbalanced (Fig. 4).

Perspectives in non-traditional isotope studies

Comparison to classic isotope tracers in archaeology

Non-traditional isotopes are likely to provide complementary information to classic isotopes or other chemical tracers, which could help access high-resolution information on diet and mobility of past populations. Melin et al. (2014), Martin et al. (2015b) and Jaouen et al. (2016b) showed that the combination of Ca, Mg or Zn (respectively) with C isotopes in bioapatite could work in a similar way to N and C isotopes when the collagen is not preserved. Thus, information on the diet of fossil remains could be retrieved in dental enamel, which can be preserved for several millions of years, as shown by Sr radiogenic isotope studies in South African early hominins (Copeland et al. 2011, Balter et al. 2012) and even Mesozoïc animals (e.g. Martin et al. 2016). This could also apply to Zn, which is as concentrated as Sr in teeth. Knowing that mobility can generate additional variation to diet on non-traditional isotopic compositions, it would be interesting to analyse whether individuals are locals or not, using Sr radiogenic isotopic ratios. In addition, Martin et al. (2014, 2015b) showed the potential of combining Mg isotopes to trace elements studies, such as Sr/Ca ratios, which is related to the trophic level via the process of biopurification. As they

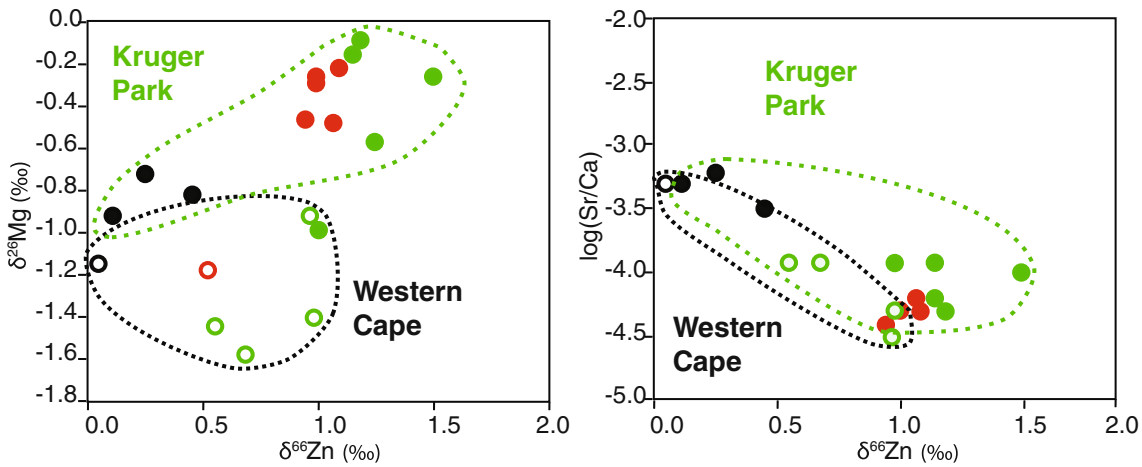

Fig. 5 Correlation between δ^{66}Zn values from Jaouen et al. (2013b) to δ^{26}Mg and Sr/Ca ratios from Martin et al. (2014). The two studies were performed on several identical specimens coming from two South African sites: Western Cape (*empty markers*) and Kruger Park (*plain markers*). *Red symbols* correspond to carnivores, *green* to herbivores and *black* to plants

worked on several specimens that we previously analysed for Zn isotopes (Jaouen et al. 2013b), we take the opportunity of this review to compare the δ^{66}Zn values, the δ^{26}Mg values and Sr/Ca ratio obtained by Martin et al. (2014). Magnesium isotopes seem to be more affected by the environmental context than Zn isotopes (Fig. 5), but within Kruger Park, some of the Zn and Mg isotopic values correlate, which might indicate that both tracers are similarly responding to the trophic level effect. The fact that both non-traditional tracers also correlate with Sr/Ca ratios could be additional evidence in favour of this conclusion (Fig. 5, Martin et al. 2014). However, in the case of Zn, the sample size is low (Fig. 5). Further work is therefore needed to confirm this pattern.

Other candidates for non-traditional isotope archaeological tracers

Some other elements have been investigated in mammalian tissues but not yet in an archaeological perspective. Mercury isotopes have been analysed in human hair and used to trace the origin of mercury in the diet (gold mining) but also the geographic origin of the fish eaten (freshwater, coastal or plain ocean) (Laffont et al. 2009, 2011; Li et al. 2014). Lithium isotopes have not yet been measured in human tissues, but it has been shown that these isotopes fractionate between the different organs of mammals (Balter and Vigier 2014), which is promising for their use as a future new dietary tracer. Analytical protocols for non-traditional isotope compositions of other elements (e.g. cadmium, silicon, selenium) have been developed in biogeochemistry but have not yet been applied to mammalian tissues.

Concluding remarks

Non-traditional isotopes have demonstrated their promising potential for archaeology, especially because they can be used to trace the diet and mobility of ancient hominins, even when collagen is not preserved. The main information provided by these tracers is summarized in Table 2. However, this field in still in its infancy and further work is needed to calibrate the tracers and to start routinely using them in the archaeological sciences. The term "non-traditional" will probably soon be outdated. It might therefore be interesting to rename these isotopes in the future, possibly according to their group in the periodic classification.

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